(12) **EUROPEAN PATENT SPECIFICATION**

(54) **Continuous bulk polymerization process for preparing a copolymer of an aromatic vinyl monomer and maleic anhydride.**

(73) Proprietor: DAICEL CHEMICAL INDUSTRIES, LTD.
No. 1, Teppo-cho
Sakai-shi Osaka-fu (JP)

(72) Inventor: Tanaka, Atsushi
940, Shinzaike, Aboshi-ku
Himeji-shi, Hyogo (JP)
Inventor: Chiba, Toshiyuki
3-5-1-121, Shinonome-machi
Sakai-shi, Osaka (JP)
Inventor: Miyata, Hirotaka
349-19, Sakagami, Aboshi-ku
Himeji-shi, Hyogo (JP)

(74) Representative: Patentanwälte Dipl.-Ing. A.
Grünecker, Dr.-Ing. H. Kinkeldey, Dr.-Ing. W.
Stockmair,
Dr. rer. nat. K. Schumann, Dipl.-Ing. P.H. Jakob,
Dr. rer. nat. G. Bezold Maximilianstrasse 58
D-8000 München 22 (DE)

Description

This invention relates to a continuous bulk polymerization process for preparing a styrene type copolymer. More specifically, the present invention relates to an improvement in a production process of an aromatic vinyl monomer-maleic anhydride copolymer having a uniform copolymer composition by continuous bulk-copolymerization. The present invention provides a process for producing a copolymer resin in which the proportion of maleic anhydride to the aromatic vinyl monomer-maleic anhydride copolymer is up to 40% by weight and which has suitable properties as a thermoplastic material.

A styrene-maleic anhydride copolymer having a composition by weight of about 50:50 has been produced on an industrial scale for a fairly long period of time and hence, has been well known as a water-soluble polymer. However, resins belonging to this group are not suited for the use as a thermoplastic material because they involve problems in regard to their water absorbance and moldability. As a plastic material for molding, copolymers containing 5 to 40% by weight, preferably 5 to 30% by weight, of maleic anhydride are suitable. Because of high heat deformation resistance, these resins have drawn increasing attention in recent years. As is well known in the art, however, in the radical copolymerization reaction between styrene and maleic anhydride, a so-called "alternating copolymer" is apt to be formed in which styrene and maleic anhydride are polymerized alternately to one another. Hence, it is not so easy to produce the above-mentioned random copolymer having a relatively small maleic anhydride content under such a condition as to provide a copolymer having a uniform composition.

In other words, the monomer ratio required for providing a copolymer having an intended composition can be calculated from the known theory of copolymerization. Nonetheless, in order to obtain the abovementioned copolymer having a composition in which the maleic anhydride content is smaller than 40% by weight, copolymerization must generally be started from a monomer mixture having a composition in which the proportion of maleic anhydride is extremely small and moreover, maleic anhydride must be added sequentially in accordance with the progress of the copolymerization in order to produce a copolymer having a predetermined composition during progress of the polymerization. Batch processes have been employed at present for producing the abovementioned copolymer so as to practice these complicated polymerization techniques, and a s lution-precipitation process has principally been used. An aqueous suspensi n p lym rization process and an emulsion p lymerization process, that are frequently employed on an industrial scale, can not be employed in this case because maleic anhydride reacts with water.

The batch type solution-precipitation polymerization process requires considerable quantities of solvent so that the rate of polymerization generally tends to be lower, and a considerable quantity of polymerization initiator is required to adjust the rate of polymerization. Hence, this process involves the drawbacks that impurities, such as the solvent and the precipitation-granulating agents, that is, a suspension-stabilizer, tend to remain inside the polymer and since these impurities are difficult to remove, coloration of the resin tends to occur when the resin is heated. From the aspect of production efficiency, too, lowering of the volume efficiency is unavoidable and fluctuation of polymer qualities tends to occur between lots because it is a batch process.

If such a copolymer resin could be produced in accordance with a continuous bulk polymerization process, the process would undoubtedly be extremely advantageous in the aspects of production cost, quality of the product and stability of the quality. The technical problems to be solved in this instance, are to find out rational operation procedures for ensuring the uniform copolymer composition as described already and to establish the required process.

A number of patents have been filed and have become known to the public in regard to continuous bulk polymerization processes of various vinyl monomers, both process-wise and apparatus-wise. According to these patents, however, there yet remains the aforementioned problem that the copolymer composition tends to become non-uniform during the progress of polymerization. However, these patents hardly teach or suggest the production techniques of the continuous bulk polymerization of the aromatic vinyl monomer-maleic anhydride copolymer. Among them, a patent application entitled "Continuous Bulk Polymerization Process" is laid open to the public as Japanese Patent Laid-Open No. 119786/1976 (applicant: Bayer A.G.). The gist of this patent application is as follows.

In continuous production of a thermoplastic molding composition consisting of:

A. 22 to 96 mol % of styrene or α-methylstyrene;

B. 0 to 78 mol % of a mono-olefinic monomer containing a nitrile group; and

C. 0 to 50 mol % of a mono-olefinic unsaturated monomer different from said monomer B;

a continuous production process characterized by th steps of:

copolymerizing, at the first stage, a monomer mixture of a mixing rati of A_1, B_1 and C_1 to a conversion of 10 to 60 mol % inside a tank

reactor, in which a continuous flow is ideally mix d, for a predetermin d average residence tim and mixing tim in the presenc f an initiator having a specific half-life time;

adding, at the second stage, a monomer mixture of a mixing ratio of A_2, B_2 and C_2 (where the sum of the mol % of A_1, B_1 and C_1 and that of A_2, B_2 and C_2 are 100, respectively), an initiator and the like; and

causing, at the third stage, the reaction mixture to flow over the entire capacity of a completely-dismountable, self-cleaning type polymerization kneader, carrying out continuous polymerization in the homogeneous phase of the bulk while reverse-mixing at the predetermined temperature for the predetermined residence time and mixing time, and continuously withdrawing the residual monomer till the residual monomer content becomes below 0.5% by weight by applying vacuum or by blowing an inert gas.

As can be seen clearly from the above-mentioned gist of the invention, this prior patent application may be evaluated as an improved technique which applies a novel contrivance to the addition of the monomer mixture and the initiator at the second stage while paying specific attention to the adjustment of the copolymer composition in the continuous bulk polymerization. However, the use of the completely-mixing type kneader polymerization reactor at the third stage would, on the contrary, further complicate the variance of the copolymer composition. In the case of the copolymerization of styrene-maleic anhydride, for example, maleic anhydride, which is consumed faster with the progress of polymerization, must be added sequentially. If the polymerization is carried out using the perfect mixing type reactor in which polymerization solutions having different propagation rates of polymerization are being mixed, the fluctuation of the composition would become extremely great and complicated, thus forming a copolymer product having a wide distribution of compositions even if the average residence time is shortened.

Example 6 of the prior patent application illustrates the production of a styrene–maleic anhydride copolymer, but it is rather difficult to believe that a transparent resin having excellent properties could be formed under the conditions set forth in this example.

Instantaneously-formed copolymer compositions are calculated for monomer mixtures of a few composition ratios using the Q.e values of styrene and maleic anhydride, which Q.e values are well known from the copolymerization theory, and changes of the compositions with the progress of polymerization are calculated. The results are shown in Figur 1. Drastic changes in the maleic anhydride content can be obviously seen, and it is easy to anticipat that the total reaction product of the co-

polymerization system having such a significant change in the composition would be heterogeneous in composition. As a matter of fact, th inventors of the present invention repeated this Example 6 under substantially the same conditions and could obtain only an extremely opaque, heterogeneous reaction product. Moreover, the precipitated polymer due to the heterogeneous composition was attached to the wall of the reactor in considerable quantities and the result of the repeated example was really unsatisfactory.

Next, in the continuous bulk polymerization process, a process using an apparatus of the perfect mixing type, that is, of a continuously stirred tank for highly viscous substances at the first stage and a horizontal (surface-renewal type) apparatus for highly viscous substances at the second and/or the third stage is known from Japanese Patent Publication No. 46871/1978 (applicant: Mitsubishi-Jukogyo K.K.), for example. The polymerization reaction is performed using plural, horizontal, parallel, rotary shafts, on each of which are mounted plurality agitation plates and the shafts are rotated in opposite directions inside a cylinder. The prior invention relates to a polymerization process characterized in that a non-solvent (mainly water) having a boiling point lower than that of the polymerization solution is sprayed in an adjusted quantity, is evaporated and is withdrawn outside the cylinder so as to carry out the polymerization reaction under the adjusted temperature condition. The prior invention relates also to a process for producing a polymer characterized in that the polymer obtained by the abovementioned process is fed into a cylinder, in which plural rotary shafts, arranged horizontally in parallel to one another and equipped with plural agitation blades, are rotated in opposite directions to one another, and volatile substances are removed by heating while the inside of the cylinder is preferably held under reduced pressure.

As is obvious from these disclosures, the horizontal apparatus for processing highly viscous substances is adapted to the process for improving the heat-removing efficiency of the polymerization solution in the continuous bulk polymerization and the removing efficiency of the volatile substances by utilizing the characteristic of the liquid surface renewing action of the highly viscous liquid. The procedures of spraying and evaporating the water is in perfect conformity with this concept. In other words, the process of this prior invention pays no consideration at all to the maintenance of the uniform copolymer composition to which the present invention is directed.

As described in detail in the foregoing, hardly any process techniques are known concerning the continuous bulk polymerization of a copolymer of an aromatic vinyl monomer and maleic anhydrid in which the monomer unit contents of the copolymer may be very constant

with respect to the progress of th polym riza-tion.

The inventors of the present invention have carried out intensive studies and have now completed the present invention.

Brief description of the drawings

Figure 1 is a graph showing the change of the composition of the instantaneously-formed polymer product with the progress of copoly-merization of styrene–maleic anhydride mixed monomers. Figure 2 is a graph showing the results of analysis of the polymerization system from the start of polymerization till the passage of about 180 minutes in accordance with the example of the present invention. Figure 3 is a flow sheet of an embodiment of a process according to the invention. In the drawing, the reference numerals identify the following elements.

1. feeding of maleic anhydride
2. feeding of aromatic vinyl monomer
3. first stage reactor
4. pump
5. horizontal reactor of one shaft
6. horizontal reactor of two shafts
7. shaft

The invention provides a continuous bulk polymerization process for preparing a co-polymer consisting of 60 to 95% by weight of an aromatic vinyl monomer and 40 to 5% by weight of maleic anhydride, which process is characterised in that in a first stage, con-tinuous bulk polymerization is carried out, using a polymerization apparatus which is a vertically stirred tank, to a conversion of 30 to 60% by continuously feeding a monomer mixture of the aromatic vinyl monomer and maleic anhydride having a feed composition ratio corresponding to the composition of the copolymer, and in a second stage, and in a third stage if necessary, continuous bulk polymerization is carried out to a conversion of 40 to 95%, using a horizontal apparatus for processing highly viscous sub-stances, equipped with one or two rotary shafts having agitation blade frames or agitation blades mounted thereon, by continuously and dividedly feeding maleic anhydride from a plurality of feed ports disposed on said apparatus for processing highly viscous sub-stances, according to formula (III), provided that each calculated value may vary within an allowance of ±20%:

amounts of maleic anhydride to be added=

$$\frac{Z_0(1-C_0)(1-\dfrac{P_1}{X})\tau r'}{(\dfrac{P_1}{X}\tau r'+1)^n} \qquad (III)$$

where:

Z_0: amount of solution fed to second or third stage polymerization apparatus

C_0: p rc ntag of polymer c ntent in the solu-tion fed to second or third polymerization apparatus

n: the number of tanks (n: 1, 2, ... n, the maxi-mum of n corresponds to the number of stages of the complete mixing)

P_1: percentage of aromatic vinyl monomer in copolymer in second or third stage of poly-merization apparatus (weight ratio)

X: average percentage of aromatic vinyl mono-mer in monomers in second or third stage polymerization apparatus (weight ratio)

τ: residence time (hr)

r': rate of polymerization (Kg/Kg/hr)

Next, the process of the present invention will be outlined. First, in performing the con-tinuous polymerization, the stage of shifting to continuous operation from the start-up of the polymerization becomes a subject of con-sideration. One of the ideas is to employ those procedures which are customarily employed for the continuous polymerization and which com-prise the steps of continuously introducing a monomer mixture having a predetermined com-position into a polymerization apparatus, heating the monomer mixture while it is flowing through the apparatus, maintaining a per-centage of solid content (conversion) after the percentage of the solid content in a prepara-tory polymerization tank reaches a predeter-mined value, adjusting the monomer com-position to such a mixing ratio as to provide a desired copolymer composition and intro-ducing the monomer mixture. In the case of the copolymerization system of the present in-vention, in which fluctuation of the copolymer composition is substantial as described above, it is preferred to employ the following pro-cedures in order to reach the steady state within a relatively short period of time.

A monomer mixture having such a composi-tion ratio as to form an instantaneously-formed copolymer having a predetermined com-position calculated from the values of the monomer reactivity ratios r_1 and r_2, which reaction ratios are well known from the copoly-merization theory, is fully charged into the first stage (preparatory) polymerization tank, is then heated to a predetermined temperature thereby to initiate the polymerization. Immediately thereafter, maleic anhydride is sequentially added at intervals 40 minutes or shorter in the amounts calculated from the following equation (1) until the polymerization proceeds to a pre-determined percentage of solid content (con-version) within the range of 30 to 60% by weight.

Amount of maleic anhydride to b sequ ntially added=

$$W_0 \cdot r \cdot (1-\frac{P_1}{K_1}) \cdot (1-\frac{P_1}{K_1} \cdot r)^{m-1} \qquad (I)$$

where
W_0: total monomer amount initially fed (Kg)
r: rate of polymerization (Kg/Kg/unit time)
K_1: percentage of aromatic vinyl monomer in the monomer initially fed (weight ratio)
P_1: percentage of aromatic vinyl component in the formed copolymer (weight ratio)
m: frequency of addition of maleic anhydride.

After the reaction system reaches the predetermined steady percentage of the solid content, it is preferred to start the continuous polymerization by immediately and continuously introducing the monomer mixture, having the composition calculated by the equation (II-a) below, in the amount calculated by the equation (II-b) below, while keeping the temperature at the predetermined temperature, continuously withdrawing the same amount of the polymerization solution and transferring it to the polymerization apparatuses of the second and subsequent stages. In this case, it is of course possible to mix and introduce a small amount of a solvent together with the monomer mixture.
Monomer composition ratio to be continuously introduced (weight ratio):

$$\frac{Sa}{Ma} = \frac{K_1 - P(K_1 - P_1)}{1 - K_1 + P(K_1 - P_1)} \quad \text{(II-a)}$$

Amount of feed introduced:

$$W \cdot r \cdot (1/P - 1)/t \quad \text{(II-b)}$$

Sa/Ma: aromatic vinyl-maleic anhydride monomer composition weight ratio to be continuously introduced
P: polymer conversion under steady state conditions (solid content)
W: total feed quantity (same as W_0 of eq. (I))
r: rate of polymerization (Kg/Kg/unit time)
t: the same time as that used as the unit of the rate of polymerization r
P_1, K_1: same as those of eq. (I)

This first stage (preparatory) reaction vessel is a vertical-agitation-system, polymerization reactor equipped with a monomer feed port, a discharge port for the polymerization solution, an agitator and means for transferring the heat of reaction (jacket, and/or cooling coil, etc.). As the agitator or stirrer, it is preferred to use various blade types, such as a turbine type, a fan turbine type, an astern blade type, Boulmagine type, a helical band blade type, a helical shaft type (equipped with a draft tube), and so forth. The polymerization temperature is generally from 80 to 160°C, preferably from 100 to 150°C. Satisfactory results could be obtained if the polymerization pr ssure is from 0 to 1.96 bar in terms f gaug pressure.
Th solid content (conversi n) in th first stag polymerization tank (pr paratory poly-

merization tank), before shifting the continuous polymerization, is to be suitably selected in accordance with th agitation capacity of the tank and its heat-r moving capacity. It is generally selected within the range of 30 to 60%. The average residence time of the monomer mixture fed continuously should be decided in conjunction with the equation (II-b), but it is generally within the range of from 0.2 to 10.0 hours. As another embodiment of the invention, the first stage of the polymerization may use two or more vertical reactors.
As the apparatus to be used at the second stage, and at the third stage, if necessary, the use of an agitation tank would quite naturally be considered in view of the addition of the monomer. However, as the conversion (solid content) rises the viscosity of the system becomes extremely high. For example, the viscosity of the system at the solid content (%) of near 80% is as high as 1,000 to 3,000 Pa.s. For this reason, agitation by means of vertical shafts suspended from the upper portion of the tank is nearly impossible so that removal of the reaction heat as well as temperature control become extremely difficult. In addition, it becomes difficult to mix rapidly and uniformly the monomer to be added to the reaction system and thus to prevent the drastic change of the composition. After all, not just a couple, but a great number, of tanks of small capacity must be connected to one another. Such an arrangement would naturally lead to a great economical disadvantage.
The inventors of the present invention have come to accomplish the present invention by using a horizontal apparatus for processing highly viscous substances, as a polymerization apparatus, which is furnished with agitation force capable of agitating high viscosity materials and which provides substantially the same effect as is brought forth by a number of small tanks connected to one another.
The one-shaft type and the two-shaft type are available for use as such a horizontal reaction apparatus and the shape and number of blades to be fitted to the shaft are disclosed in Japanese Patent Publication Nos. 12484/1970, 22449/1967 and 20433/1971, U.S. Patent No. 2,758,915, Japanese Patent Publication Nos. 16901/1969, 40732/1974 and 46871/1978, and Japanese Patent Laid-Open Nos. 102894/1973 and 86590/1975, for example. Hence, they should be selected suitably in accordance with the conditions of the polymerization reaction, the viscosity of the system, and so forth. The preferred number of blade frames or blades per unit is from 2 to 40. Since the shaft equipped with such a number of blades or blade frames is sufficiently supported by both ends of th apparatus, it is capable of sufficiently agitating the polym rization soluti n. Moreover, this agitation ffects ne form of agitati n to tak place insid a perfectly mixed tank in the dir ction at right angles

to the shaft, that is to say, within the zones partitioned by the blades or the blade frames, and the other form of a piston flow with respect to the apparatus as a whole, that is to say, in the axial direction.

Realizing the feature of the apparatus, the present invention contemplates utilizing the apparatus for controlling the copolymer composition of a copolymer. This is one of the essential features of the present invention. In other words, one of the essential points of the present invention resides in that maleic anhydride, in amounts calculated by the following equation (III), is continuously added to the polymerization solution flowing continuously through such a horizontal apparatus in each polymerization zone partitioned by the blades or blade frames in order to facilitate the accurate control of the copolymer composition.

Amounts of maleic anhydride to be added=

$$\frac{Z_0(1-C_0)(1-\frac{P_1}{X})\tau r'}{(\frac{P_1}{X}\tau r'+1)_n} \quad (III)$$

where:

Z_0: amount of solution fed to second or third stage polymerization apparatus

C_0: percentage of polymer content in the solution fed to second or third polymerization apparatus

n: the number of tanks (n: 1, 2 ... n, the maximum of n corresponds to the number of stages of complete mixing)

P_1: percentage of aromatic vinyl monomer in copolymer inside second or third stage polymerization apparatus (weight ratio)

X: average percentage of aromatic vinyl monomer in monomers inside second or third stage polymerization apparatus (weight ratio)

τ: residence time (hr)

r': rate of polymerization (Kg/Kg/hr)

It is possible to add maleic anhydride in the amounts calculated by the abovementioned equation (III) to the polymerization solution in each polymerization zone by spraying or injecting it from a feed port at the upper portion of the apparatus or from a pressure-feed port at the lower portion of the apparatus.

Generally speaking it is preferred to select operating conditions such that when a conversion of the monomers to the polymer under the steady state conditions in the first stage polymerization tank is from 30 to 60%, it is from 40 to 80% in the second stage apparatus and from 60 to 95% in the third stage apparatus. It is suitable to carry ut the poly-

merization at the second stage and/or the third stag at the temperature within the range of 80 to 180°C, preferably 100 to 160°C. The polymerization can be carried out at a considerably reduced pressure or a considerably elevated pressure inside the polymerization apparatus and a pressure within the gauge pressure of —0.78 to 2.94 bar is preferred.

The foregoing description has dealt with the case wherein only maleic anhydride is to be supplemented, with reference to the equations (I) and (III), in order to adjust the composition of the resulting copolymer because maleic anhydride is consumed relatively quickly in the copolymerization system. Since maleic anhydride is solid at room temperature and is hygroscopic, however, it is not so easy to feed quantitatively. Accordingly, in most cases, it is more advantageous to feed the monomer in the solution form, if possible. In such a case, it is also possible to introduce a maleic anhydride solution in an amount corresponding to the amount calculated from the equations (I) and (III) by dissolving maleic anhydride in toluene or ethylbenzene, for example, Nonetheless, it is often undesirable that such an inert third component, that is to say, the solvent, is present in the polymerization system in great quantities. To cope with this problem, it is also possible to add maleic anhydride as a solution dissolved in the aromatic vinyl monomer, that is to say, as the monomer mixture, containing a desired amount of maleic anhydride. In this case, the copolymerization system would naturally become further complicated so that the following conditions are necessary:

(A) Mixed monomer composition: maleic anhydride/aromatic vinyl monomer (weight ratio) must fall within the range of 11/89 to 99/1.

(B) The residence time in each completely mixed tank of the second and third polymerization apparatuses must be almost constant and equal to one another.

On the above-mentioned conditions, the mixed monomer amount calculated from the following equation may be introduced additionally.

Mixed monomer amount to be additionally supplemented at the start of the first stage polymerization tank=

$$W_0 \cdot K_1 \cdot \{1-r+(\frac{K_1-P_1}{K_1-G})r\}^{m-1} \cdot (\frac{K_1-P_1}{K_1-G}) \cdot r$$

where

G: p rcentag of aromatic vinyl monomer in mixed monomer to be additi nally supplemented

Mixed monomer amount t be supplemented in second and third stage polymerization apparatuses=

$$Z_0(1-C_0)\,(1-\frac{P_1}{X})\cdot\tau\cdot r'(1-\frac{G}{X})^{n-1}\cdot\{(1+\frac{P_1}{X}\cdot\tau r')-\frac{G}{X}(1+\tau\cdot r')\}^{-n}$$

where the symbols have the same meaning as defined in the equation (I) or (III).

If it is troublesome to introduce a monomer or mixed monomers in the amount calculated from the above, per each perfectly mixed tank, or if there is any restriction in the used apparatus, it is preferable that 2 to 5 of said perfectly mixed tanks are considered to form one block. The average value of the amount of monomer as described above, for the entire block, of the amounts obtained above is added to each completely mixed tank. Alternatively the total amount, as summed for said block, of the monomer is added at one port of said block. In either case, the number of blocks is two or more.

After all, consideration should be made so that the addition amount of maleic anhydride has progressively decreasing gradients for the whole polymerization system.

As discussed above, the process exactly operated according to the above shown formulae, I, IIa, IIb, III and variations thereof can obtain the best result. It is permitted in the invention, however, that each calculated value of monomer amounts may vary within a range of up to 20%, preferably 10%, above or below from the value calculated by the formula.

The polymerization solution that contains a high solid content and has been taken out from the second or third stage polymerization apparatus is transferred to an evaporator to remove and recover volatile components while the polymer, as the solid content, is passed through an extruder and is thus granulated. There is no specific restriction on these post-treatment steps and suitable instruments or apparatuses may be suitably selected in accordance with the final shape of the resin or with the target value of the residual volatile components. As the evaporator, it is preferred to employ a centrifugal membrane (thin film) evaporator, for example.

As the aromatic vinyl monomer to be used in the present invention, styrene, α-methyl-styrene and halogenated styrene or their mixtures can be illustrated.

According to the invention, there may be used a third monomer, other copolymerizable monomers such as acrylonitrile, acrylic acid and its ester, for example methyl ester, methacrylic acid and its ester, for example methyl ester, and a rubber-like polymer ingredient such as polybutadiene and styrene-butadiene rubber. Two or more kinds of the third monomers may be used. The amount of the third monomer is preferably from 0 to 30 wt. %, based on the total amount of th monom r.

In practising the polymerizati n f th

present invention, it is possible to add suitable amounts of a polymerization initiator or a molecular weight-adjusting agent. However, if the purity of the copolymer resin is a critical issue, it is better not to use these agents, or, even if they are used, their amounts be reduced to the greatest possible extent. The solvent, which is to be added to the system, whenever necessary, is preferably an hydrocarbon inert to the polymerization system, such as benzene, toluene, xylene, ethylbenzene, p-cymene and the like, but there is no restriction on the solvent, in particular.

The viscosity of the solution of the aromatic vinyl monomer-maleic anhydride copolymer obtained in accordance with the process of the present invention may be from 0.5 to 1.0, preferably 0.6 to 0.9 d/g. The solution viscosity (sp/c) is measured in a tetrahydrofuran solution (0.5 wt. % conc.) at 30°C.

Hereinafter, an example of the present invention will be illustrated.

Example

100 Kg of a styrene-maleic anhydride monomer mixture having a mixing ratio (weight ratio) of 0.993/0.007 was fed into a first stage polymerization tank (preparatory polymerization tank) having a helical band type agitator and was heated to 140°C with stirring in a nitrogen stream. After 10 minutes from the elevation of the temperature to 140°C, 0.56, 0.53, 0.50, 0.48 and 0.45 Kg of maleic anhydride were added in intervals of each 10 minutes. These amounts were calculated from the equation (I) with the rate of reaction r=0.06 (Kg/Kg/10 min.). At the time when the addition of maleic anhydride was completed at 50 minutes from the start, a styrene-maleic anhydride monomer mixture having a mixing ratio (weight ratio) of 0.965/0.035 was continuously introduced at a rate of 85.8 Kg/hr and the polymer solution in substantially the same amount was withdrawn and was transferred to the second stage polymerization apparatus. The monomer composition and the feed amount were calculated from the equations (II-a) and (II-b) with r=0.06 (Kg/Kg/10 min.) in the same way (with the proviso that P_1=0.9).

During the period from the start of the polymerization until the passage of about 180 minutes, samples in limited amounts were collected and analyzed with the results shown in Figure 2. It can be seen from the drawing that the maleic anhydride content (about 10%) in the resulting polym r and the solid content (about 30%) after shifting to the continuous polym rization were adjusted extremely well to a constant value. As a matter of fact, the

polym r solution withdrawn from the first stage (preparatory) polymerization tank was extremely transparent and it could be observed obviously that no polymer having an abnormal copolymer composition was formed during polymerization.

As the second stage polymerization apparatus, there was employed one which had one horizontal shaft equipped with 10 equidistant circular blades.

The third stage polymerization apparatus was a type including two shafts fitted alternately with 22, in total, of frame-type blades rotating in the same rotating direction. The polymerization conditions were set assuming that each apparatus was a reactor having 11 perfectly mixed tanks.

While the polymerization solution was being transferred from the first stage polymerization tank to the second polymerization tank at a rate of 85.8 Kg/hr, maleic anhydride was continuously added to the successive perfectly mixed tanks at the rates of 0.277, 0.265, 0.253, 0.241, 0.230, 0.220, 0.210, 0.201, 0.191, 0.183 and 0.174 Kg/hr, respectively. While this polymerization solution (conversion under the steady state of 54.8%) was being transferred to the third stage polymerization tank at a rate of 88.2 Kg/hr, maleic anhydride was continuously added at the successive perfectly mixed tanks in the third polymerization tank at rates of 0.167, 0.159, 0.152, 0.145, 0.138, 0.132, 0.126, 0.120, 0.115, 0.109 and 0.104 Kg/hr, respectively. The solid content in the polymerization solution discharged from the third stage polymerization stage was 70.3% and the maleic anhydride content in the formed copolymer was 10.3%. The polymerization temperature was 140°C at both second and third stages.

The addition amounts of maleic anhydride in the second and third stage polymerization tanks were calculated from the aforementioned equation (III) (with the proviso that $P_1=0.9$, $K_1=0.9966$, $\tau=0.15$ hr, $r=0.354$/hr).

As can be appreciated from the abovementioned results, the solid content in the polymerization mixture is very high and the composition of the styrene-maleic anhydride copolymer obtained in accordance with the process of the present invention is uniform and transparent and has the intended composition (maleic anhydride 10%). The viscosity of the solution was 0.72 dl/g.

Claims

1. A continuous bulk polymerization process for preparing a copolymer consisting of 60 to 95% by weight of an aromatic vinyl monomer and 40 to 5% by w ight of maleic anhydride, characterised in that in a first stag , continuous bulk polymerization is carried out, using a p lymerization apparatus which is a vertically stirred tank, to a conversion of 30 to 60% by

continu usly feeding a monomer mixture of the aromatic vinyl monomer and maleic anhydrid having a feed composition ratio corresponding to the composition of the copolymer, and in a second stage, and in a third stage if necessary, continuous bulk polymerization is carried out to a conversion of 40 to 95%, using a horizontal apparatus for processing highly viscous substances, equipped with one or two rotary shafts having agitation blade frames or agitation blades mounted thereon, by continuously and dividedly feeding maleic anhydride from a plurality of feed ports disposed on said apparatus for processing highly viscous substances, according to formula (III), provided that each calculated value may vary within an allowance of ±20%:

Amounts of maleic anhydride to be added=

$$\frac{Z_0(1-C_0)(1-\dfrac{P_1}{X})\tau r'}{(\dfrac{P_1}{X}\tau r'+1)^n} \qquad (III)$$

where:

Z_0: amount of solution fed to second or third stage polymerization apparatus

C_0: percentage of polymer content in the solution fed to second or third polymerization apparatus

n: the number of tanks (n: 1, 2 ... n, the maximum of n corresponds to the number of stages of the complete mixing)

P_1: percentage of aromatic vinyl monomer in copolymer in second or third stage polymerization apparatus (weight ratio)

X: average percentage of aromatic vinyl monomer in monomers in second or third stage polymerization apparatus (weight ratio)

τ: residence time (hr)

r': rate of polymerization (Kg/Kg/hr)

2. A process as claimed in claim 1, wherein the reaction temperature in the first stage is in the range between 80°C and 160°C, and in the second and third stages is in the range between 80°C and 180°C.

3. A process as claimed in claim 1, wherein both said monomers are fed according to formulae (IIa) and (IIb) in the continuous condition of the first stage, provided that each calculated value may vary with an allowance of 20%:

$$\frac{Sa}{Ma} = \frac{K_1-P(K_1-P_1)}{1-K_1+P(K_1-P_1)} \qquad (II\text{-}a)$$

Amount of f ed introduced:

$$W \cdot r \cdot (1/P-1)/t \qquad (II\text{-}b)$$

Sa/Ma: aromatic vinyl-maleic anhydride mono-
mer composition weight ratio to be con-
tinuously introduced

P: polymer conversion under steady state con-
ditions (solid content)

W: total feed quantity (Kg)

r: rate of polymerization (Kg/Kg/unit time)

t: the same time as that used as the unit of the
rate of polymerization r

P_1: percentage of aromatic vinyl component in
the formed copolymer (weight ratio)

K_1: percentage of aromatic vinyl monomer in
the monomer initially fed (weight ratio)

4. A process as claimed in claim 1, wherein
maleic anhydride is fed in the first stage accord-
ing to formula (I) until the steady condition has
been attained, provided that the amount may
vary within an allowance of 20% above or
below the calculated value:

Amount of maleic anhydride to be added=

$$W_0 \cdot r \cdot (1 - \frac{P_1}{K_1}) \cdot (1 - \frac{P_1}{K_1} \cdot r)^{m-1} \quad (I)$$

where

W_0: total monomer amount initially fed (Kg)

r: rate of polymerization (Kg/Kg/unit time)

K_1: percentage of aromatic vinyl monomer in
the monomer initially fed (weight ratio)

P_1: percentage of aromatic vinyl component in
the formed copolymer (weight ratio)

m: frequency of addition of maleic anhydride.

5. A process as claimed in claim 1, wherein
two or more vertical reactors are used in the
first stage.

Patentansprüche

1. Kontinuierliches Massenpolymerisations-
verfahren zur Herstellung eines aus 60 bis 95
Gew.-% eines aromatischen Vinylmonomeren
und 40 bis 5 Gew.-% Maleinsäureanhydrid
bestehenden Copolymers, dadurch gekenn-
zeichnet, daß in einer ersten Stufe unter Ver-
wendung eines senkrecht gerührten Gefäßes als
Polymerisationsvorrichtung durch kontinuier-
liches Einspeisen einer Monomerenmischung
aus dem aromatischen Vinylmonomer und
Maleinsäureanhydrid mit einem der Zusammen-
setzung des Copolymers entsprechenden Ein-
speisungszusammensetzungsverhältnis eine kon-
tinuierliche Massenpolymerisation bis zu einer
Umwandlung von 30 bis 60% durchgeführt
wird, und in einer zweiten Stufe und, falls
erforderlich, einer dritten Stufe unter Ver-
wendung einer horizontalen Vorrichtung zur
Verarbeitung hochviskoser Substanzen, die mit
einem oder zwei Rotationsschaften mit daran
b festigten Rührblattrahmen oder Rührblättern
ausgerüstet ist, durch kontinuierliches und
geteiltes Einspeisen von Mal insäureanhydrid
aus einer Vielzahl von an der Vorrichtung zur

Verarbeiting hochviskoser Substanzen ange-
ordneten Einspeiseöffnungen gemäß Formel (III),
w bei gilt, daß jeder berechn t Wert inn r-
halb einer zulässigen Abw ichung v n ±20%
variieren kann, eine kontinuierliche Massen-
polymerisation bis zu einer Umwandlung von
40 bis 95% durchgeführt wird:

Mengen an zuzusetzendem Maleinsäurean-
hydrid=

$$\frac{Z_0(1-C_0)(1-\frac{P_1}{X})\tau r'}{(\frac{P_1}{X}\tau r'+1)^n} \quad (III)$$

worin bedeuten:

Z_0: Menge der Lösung, die der Polymerisa-
tionsvorrichtung in der zweiten oder dritten
Stufe zugeführt wird

C_0: Prozentgehalt des Polymergehaltes in der
Lösung, die der zweiten oder dritten Poly-
merisationsvorrichtung zugeführt wird

n: Anzahl der Gefäße (n: 1, 2 ... n, das Maxi-
mum von n entspricht der Anzahl von Stufen
der vollständigen Durchmischung)

P_1: Prozentgehalt an aromatischem Vinyl-
monomer im Copolymer in der Polymerisa-
tionsvorrichtung der zweiten oder dritten
Stufe (Gewichtsverhältnis)

X: Durchschnittlicher Prozentgehalt an aroma-
tischem Vinylmonomer in den Monomeren in
der Polymerisationsvorrichtung der zweiten
oder dritten Stufe (Gewichtsverhältnis)

τ: Verweilzeit (h)

r': Polymerisationsgeschwindigkeit (kg/kg/h)

2. Verfahren nach Anspruch 1, dadurch ge-
kennzeichnet, daß die Reaktionstemperatur in
der ersten Stufe im Bereich zwischen 80 und
160°C und in der zweiten und dritten Stufe im
Bereich zwischen 80 und 180°C liegt.

3. Verfahren nach Anspruch 1, dadurch ge-
kennzeichnet, daß beide Monomere gemäß den
Formeln (II a) und (II b) im kontinuierlichen
Zustand der ersten Stufe eingespeist werden,
wobei gilt, daß jeder berechnete Wert inner-
halb einer zulässigen Abweichung von ±20%
variieren kann:

$$\frac{Sa}{Ma} = \frac{K_1-P(K_1-P_1)}{1-K_1+P(K_1-P_1)} \quad (II\ a)$$

Menge der zugeführten Einspeisung:

$$W\ r\ (1/P-1)/t \quad (II\ b)$$

Sa/Ma: Gewichtsverhältnis der kontinuierlich
zuzuführenden Zusammensetzung aus aro-
matischem Vinylmonomer-Mal insäur an-
hydrid

P: Polymerumwandlung unter Bedingungen des
stationären Zustandes (Feststoffgehalt)

W: gesamte Einspeisungsmenge (kg)

r; Polymerisationsgeschwindiget (kg/kg/Zeit-
einheit)

t: die gleiche Zeit, wie als Einheit der Poly-
merisationsgeschwindigkeit r verwendet

P_1: Prozentgehalt der aromatischen Vinylkom-
ponente im gebildeten Copolymer (Ge-
wichtsverhältnis)

K_1: Prozentgehalt des aromatischen Vinyl-
monomers im anfänglich eingespeisten
Monomer (Gewichtsverhältnis)

4. Verfahren nach Anspruch 1, dadurch ge-
kenzeichnet, daß Maleinsäureanhydrid in der
ersten Stufe gemäß Formel (I) eingespeist wird,
bis der stationäre Zustand erreicht worden ist,
wobei gilt, daß die Menge innerhalb einer zu-
lässigen Abweichung von 20% über oder unter
dem berechneten Wert variieren kann:

Menge an zuzufügendem Maleinsäurean-
hydrid=

$$W_0 \cdot r \cdot (1 - \frac{P_1}{K_1}) \cdot (1 - \frac{P_1}{K_1} \cdot r)^{m-1} \quad (I)$$

worin bedeuten:

W_0: gesamte, anfänglich eingespeiste Mono-
mermenge (kg)

r: Polymerisationsgeschwindigkeit (kg/kg/Zeit-
einheit)

K_1: Prozentgehalt an aromatischem Vinyl-
monomer in dem anfänglich eingespeisten
Monomer (Gewichtsverhältnis)

P_1: Prozentgehalt der aromatischen Vinylkom-
ponente in dem gebildeten Copolymer (Ge-
wichtsverhältnis)

m: Häufigkeit der Zugabe von Maleinsäurean-
hydrid

5. Verfahren nach Anspruch 1, dadurch ge-
kennzeichnet, daß zwei oder mehr vertikale
Reaktoren in der ersten Stufe verwendet
werden.

Revendications

1. Procédé en continu de polymérisation en
masse d'un copolymère constitué de 60 à 95%
en poids d'un monomère vinylaromatique et de
40 à 5% en poids d'anhydride maléique, carac-
térisé en ce que dans un premier stade, on
effectue en continue une polymérisation en
masse, en utilisant un appareil de polymérisa-
tion qui est une cuve à agitation verticale, à une
conversion de 30 à 60% par introduction con-
tinue d'un mélange monomère du monomère
vinylaromatique et d'anhydride maléique ayant
un rapport de composition d'alimentation
correspondant à la composition du copolymère
t, dans un second stade, et dans un troisième
stade s'il est nécessaire, on effectue en continu
une polym'risation en masse à une conversion

de 40 à 95% en utilisant un appareil horizontal
pour le traitement des substances très
visqueuses, équipé d'un ou deux arbres
tournants sur lesquels sont montés des châssis
à pales d'agitation ou des pales d'agitation, par
introduction continue ou discontinue d'an-
hydride maléique par plusieurs ouvertures d'ali-
mentation disposées sur ledit appareil pour le
traitement des substances très visqueuses,
selon la formule (III), étant entendu que chaque
valeur calculée peut varier dans la limite de
±20%:

quantités d'anhydride maléique à ajouter=

$$\frac{Z_0(1-C_0)(1-\frac{P_1}{X})\tau r'}{(\frac{P_1}{X}\tau r' + 1)^n} \quad (III)$$

dans laquelle:

Z_0: quantité de solution introduite dans
l'appareil de polymérisation du second et du
troisième stade,

C_0: pourcentage de polymère contenu dans la
solution introduite dans le second ou le
troisième appareil de polymérisation,

n: nombre de cuves (n: 1, 2 ... n, le maximum
de n correspondant au nombre de stades du
mélange complet),

P_1: pourcentage de monomère vinylaromatique
dans le copolymère dans l'appareil de poly-
mérisation du second ou du troisième stade
(rapport pondéral),

X: pourcentage moyen de monomère vinylaro-
matique dans les monomères dans l'appareil
de polymérisation du second ou du troisième
stade (rapport pondéral),

τ: temps de séjour (h),

r': vitesse de polymérisation (kg/kg/h).

2. Un procédé comme revendiqué dans la
revendication 1, dans lequel la température de
réaction dans le premier stade est dans la
gamme située entre 80°C et 160°C et, dans le
second et le troisième stade, est dans la gamme
située entre 80°C et 180°C.

3. Un procédé comme revendiqué dans la
revendication 1, dans lequel lesdits deux mono-
mères sont introduits selon les formules (IIa) et
(IIb) en continu dans le premier stade, sous
réserve que chaque valeur calculée puisse varier
dans la limite de 20%:

$$\frac{S}{Ma} = \frac{K_1 - P(K_1 - P_1)}{1 - K_1 + P(K_1 - P_1)} \quad (II\text{-}a)$$

quantité d'alimentation introduite:

$$W \cdot r \cdot (1/P - 1)/t \quad (II\text{-}b)$$

Sa/Ma: rapport pondéral de composition mono-
mèr vinylaromatique-anhydride maléique à
introduir en continu

P: conversion du polymère en conditions
d'équilibre (teneur en matières sèches),

W: quantité totale d'alimentation (kg),

r: vitesse de polymérisation (kg/kg/unité de
temps),

t: même temps que celui utilisé comme unité de
la vitesse de polymérisation r,

P_1: pourcentage du composant vinylaro-
matique dans le copolymère formé (rapport
pondéral),

K_1: pourcentage du monomère vinylaro-
matique dans le monomère initialement
introduit (rapport pondéral).

4. Un procédé comme revendiqué dans la
revendication 1, dans lequel l'anhydride
maléique est introduit dans le premier stade
selon la formule (I) jusqu'à ce qu'un état
d'équilibre soit atteint, sous réserve que la
quantité puisse varier dans une limite de 20%
au-dessous et au-dessus de la valeur calculée:

quantité d'anhydride maléique à ajouter=

$$W_0 - r \cdot \left(1 - \frac{P_1}{K_1}\right) \cdot \left(1 - \frac{P_1}{K_1} \cdot r\right)^{m-1} \qquad (I)$$

dans laquelle

W_0: quantité totale de monomère initialement
introduite (kg),

r: vitesse de polymérisation (kg/kg/unité de
temps),

K_1: pourcentage de monomère vinylaromatique
dans le monomère initialement introduit
(rapport pondéral),

P_1: pourcentage de composant vinylaro-
matique dans le copolymère formé (rapport
pondéral),

m: fréquence d'addition de l'anhydride
maléique.

5. Un procédé comme revendiqué dans la
revendication 1, dans lequel deux ou plusieurs
réacteurs verticaux sont utilisés dans le premier
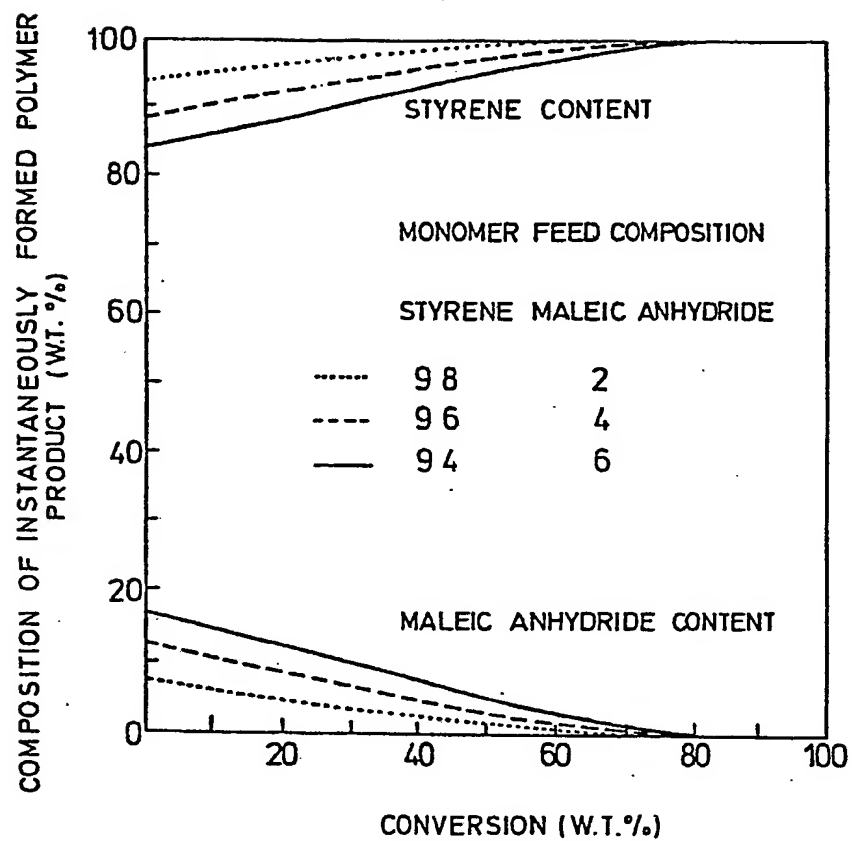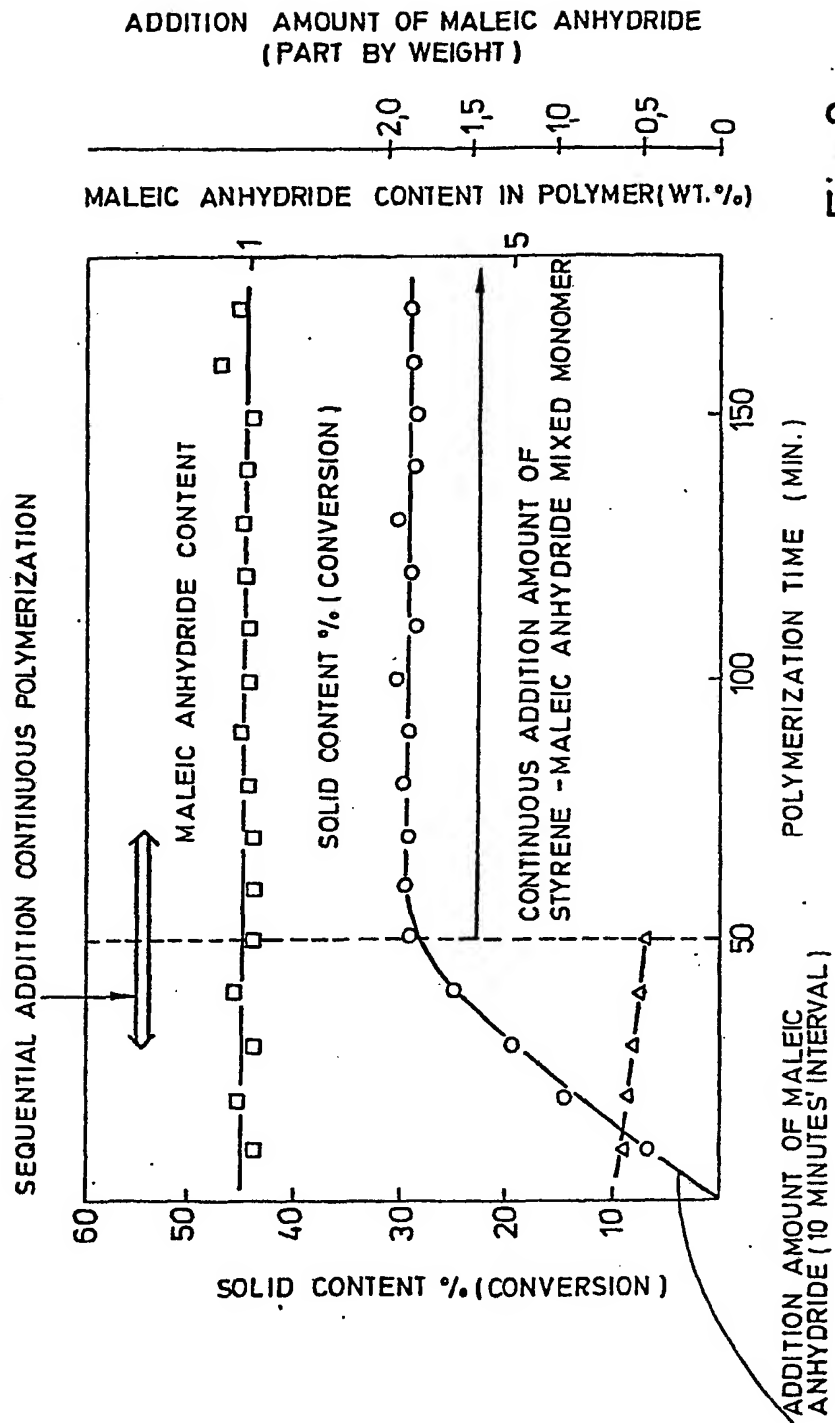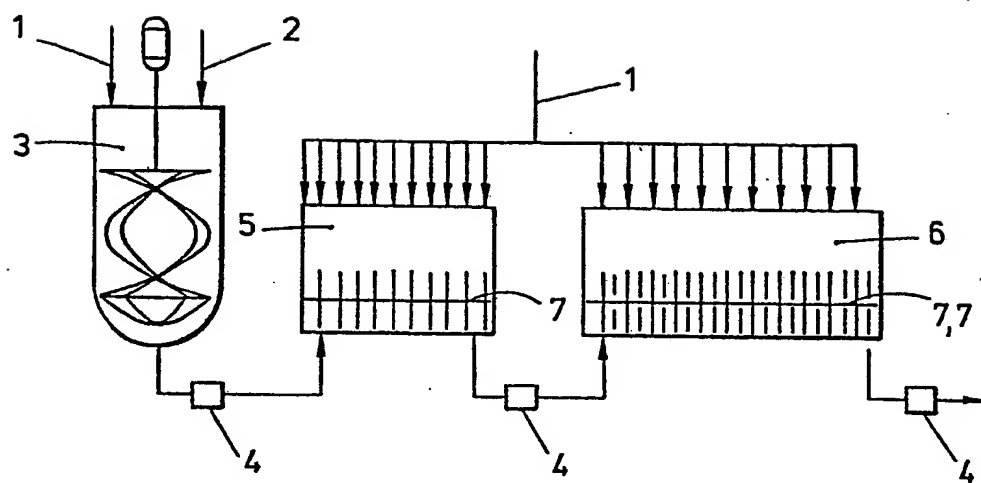stade.

5

10

15

20

25

30

35

40

45

50

55

60

65

Fig.1

Fig.2

ADDITION AMOUNT OF MALEIC ANHYDRIDE
(PART BY WEIGHT)

MALEIC ANHYDRIDE CONTENT IN POLYMER(WT.%)

SEQUENTIAL ADDITION CONTINUOUS POLYMERIZATION

MALEIC ANHYDRIDE CONTENT

SOLID CONTENT % (CONVERSION)

CONTINUOUS ADDITION AMOUNT OF
STYRENE - MALEIC ANHYDRIDE MIXED MONOMER

POLYMERIZATION TIME (MIN.)

SOLID CONTENT % (CONVERSION)

ADDITION AMOUNT OF MALEIC
ANHYDRIDE (10 MINUTES' INTERVAL)

Fig. 3